2. INSTRUMENTATION AND SAMPLE PREPARATION

as a donut cake by Merrill & Bassett (1974)], as shown in Fig. 2.7.6. In the directions perpendicular to the DAC axis, the maximum coordinate $d_{yz}^* = 2\lambda^{-1}\sin\alpha_M$ of reciprocal vectors is for many crystals larger than the resolution of the data (for a typical DAC, $\alpha_M = 40°$, which for organic crystals or other weakly scattering substances is less than required, as the data measured with Mo $K\alpha$ radiation for molecular crystals often extend up to a maximum θ of only about 25°). However, access to the reciprocal lattice is significantly limited along the DAC axis (perpendicular to the flat cushion). In this direction, only those reflections can be accessed for which

$$d_x^* = 2\lambda^{-1}\sin^2(\alpha_M/2),$$

where d_x^* is the maximum coordinate of accessible reciprocal vectors along the x_L axis running from the sample to the radiation source in the laboratory reference system, λ is the wavelength, and α_M is the opening angle of the window measured from the DAC axis (or the maximum inclination of the DAC axis to the incident beam). For example, a DAC with a full window opening angle of $2\alpha_M = 60°$ limits the laboratory reciprocal x coordinate to 0.1885 Å^{-1} when λ(Mo $K\alpha$) = 0.71073 Å is used; if the crystal x^* axis is aligned along the laboratory x_L axis, and if the crystal $a^* = 0.10$ Å^{-1}, then the maximum Bragg reflection index $|h|$ is 1. If the wavelength is decreased to λ(Ag $K\alpha$) = 0.56 Å, the maximum d_x increases to 0.2392 Å^{-1} and reflections with index $h = 2$ can be recorded.

Although the accessible region of the reciprocal lattice depends strongly on the DAC design, the final completeness of the data also depends on several other factors: (i) the symmetry of the sample crystal; (ii) the sample orientation; and (iii) the wavelength of the X-ray radiation. Therefore, the DAC is ideally suited to high-pressure studies of simple and high-symmetry crystals. The Laue-class symmetry of cubic crystals is either $m\bar{3}$ or $m\bar{3}m$, and in most cases the whole of the required resolution falls within the accessible flat-cushion reciprocal region. Thus, the completeness in high-pressure experiments on cubic samples mounted in the chamber at a random orientation is not limited. For hexagonal and tetragonal samples, the crystal orientation is very significant. The maximum completeness can be obtained when the hexagonal or tetragonal axis is perpendicular to the DAC axis. Then the sample reciprocal axis c^* is located along the flat-cushion plane. When two axes of a monoclinic or orthorhombic crystal are at 90° to the DAC axis, a considerable portion of the symmetry-independent part of the reciprocal lattice is not accessible. This reduces the completeness of the data, even though the redundancy of the data is increased. Optimum orientation of the sample can double the completeness compared with experiments measured for the same sample with its axes aligned along the DAC axis and plane.

The completeness of the data can be increased by collecting several data sets for samples oriented differently in the DAC and merging these data (Patyk *et al.*, 2012). This purpose can also be achieved by placing several crystal grains at different orientations in the high-pressure chamber, and then separating their reflections, indexing them and merging.

When the powder diffraction method is used, this problem of completeness is irrelevant. As shown in Fig. 2.7.7, for an ideal powder with randomly oriented grains all reciprocal-lattice nodes can be represented as spheres and they all satisfy the Bragg diffraction condition. The main problem occurring for samples with low symmetry and long lattice constants is overlapping reflections. The intensity of the powder reflection rings is low,
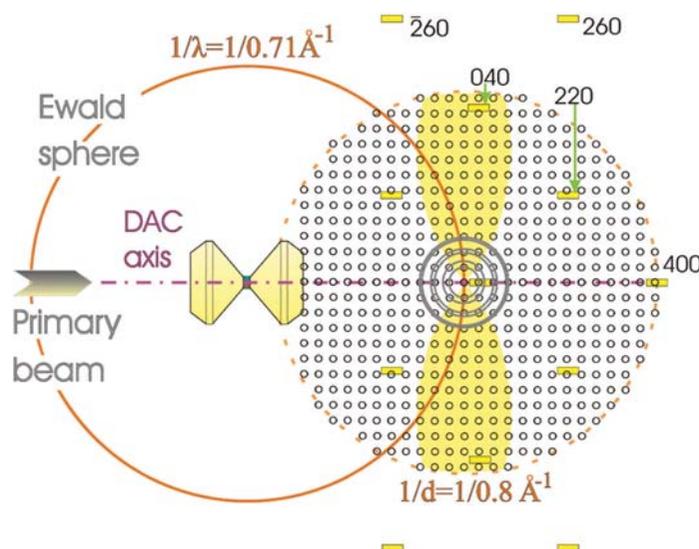
Figure 2.7.7
A schematic illustration of the reciprocal space associated with a sample enclosed in a diamond-anvil cell (DAC). For clarity, the sizes of the sample and diamond anvils have been increased. The Ewald sphere is drawn for the sample only and cubic symmetry with an a parameter of 10 Å has been assumed. Of the reciprocal lattice of the sample, only the layer of $hk0$ nodes is shown as small circles within the resolution limit of $1/d_{hkl} = 1/0.8$ Å^{-1}. The Ewald spheres of the diamond anvils have been omitted, and only the layer of nodes $hk0$ of the detector anvil is shown as yellow rectangles. Owing to its short unit-cell parameter of 3.57 Å and $Fd\bar{3}m$ symmetry, there are few diamond reflections in the pattern. Note the displaced origins of the reciprocal lattices of the sample and of the detector anvil (the anvil on the detector side) as a result of the off-centre positions of the anvil. For a powdered sample, each node is distributed on a sphere. In this drawing, the spheres are represented by circles only for nodes 100, 110, 200, 210, 220 and 300. The other node spheres contained within the chosen resolution limit have been omitted for clarity; for a triclinic sample, the $hk0$ layer would include 266 powder reflections.

because only a small fraction of the sample volume, less than one part per million, contributes to the intensity at a specific point on the reflection ring. Furthermore, the sample volume in the DAC is very small. For these reasons, powder X-ray diffraction in the laboratory usually provides only qualitative information. After the introduction of synchrotron radiation and area detectors, powder diffraction became one of most efficient methods of high-pressure structural studies.

2.7.8. Single-crystal data collection

It is essential that a crystal sample is centred precisely on the diffractometer. Optical centring of a crystal is hampered by the limited view of the sample through the DAC windows in one direction only and by the strong refractive index of diamonds. Consequently, diffractometric methods of crystal centring are more precise for DAC centring. Hamilton's method comparing the diffractometer setting angles of reflections at equivalent positions (Hamilton, 1974) was modified for the purpose of the DAC by King & Finger (1979) and then generalized for any reflections, not necessarily at equivalent positions (Dera & Katrusiak, 1999). These methods are very precise, but they require the approximate orientation matrix (UB matrix) of the sample crystal (Busing & Levy, 1967) to be known and the reflections to be indexed. This information was determined at the beginning of an experiment when traditional diffractometers with a point detector were used. However, nowadays diffractometers with area detectors are used, and generally the crystal orientation

   references